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An Investigation into a Palladium Catalyzed Hydrosilylation of Olefins

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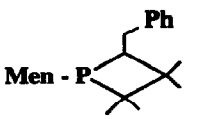
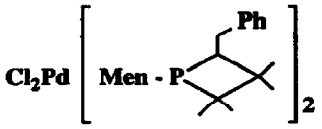
Abstract: *Hydrosilylations of styrene and cyclopentadiene are performed in the presence of phosphetane-palladium 1:1 and 2:1 complexes. An unprecedented inhibitory effect of the second phosphine ligand suggests a monophosphine-Pd catalyzed process which proceeds through four-coordinate intermediates.*

Several transition metal compounds are known to catalyze the hydrosilylation of olefinic bonds. Platinum derivatives are the best established and most efficient systems, but the related palladium based catalysts[1] have some important features. The most significant difference between the two systems lies in their regioselectivity. With the Pt catalyzed system, 1-silylalkanes are produced. In contrast, palladium catalysts lead highly selectively to 2-silylalkanes: this process creates a chiral carbon atom and permits asymmetric catalysis[2]. Any palladium precursor may be used, but they are only active in combination with phosphines [1c].

An exploratory study of the potential of phosphetane **1**[3] and its analogues as chiral ligands in transition metal catalysis led us to examine the Pd-catalyzed hydrosilylation reactions above.



1 ; *P(R) C(S)*

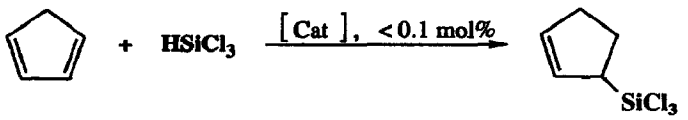


2

Men = l-menthyl

Hydrosilylation catalysts are generally prepared *in situ* by mixing phosphines and the $Cl_2Pd(PhCN)_2$ complex in a 2:1 ratio[2,4]. However, isolated (aminophosphine) $PdCl_2$ complexes have been used[5] as the catalyst precursors. For the experiments described here, *trans*-dichloro bis(4-benzyl-1-menthyl-2,2,3,3-tetramethylphosphetane) palladium (II), **2**, was prepared by addition of two equivalents of **1** to $Cl_2Pd(PhCN)_2$, in 93% yield after crystallization from pentane. After full characterization[6], it was used as a catalyst precursor in the hydrosilylations of cyclopentadiene and styrene (Scheme 1 and Table 1).

Scheme 1. Hydrosilylation reactions of Cyclopentadiene and Styrene catalyzed by Phosphetane-Palladium Complexes



(1)

$$PhCH{=}CH_2 + HSiCl_3 \xrightarrow{[Cat],\ <0.1\ mol\%} PhCH(Me)SiCl_3 \qquad (2)$$

Most of the reactions were carried out in sealed glass ampoules. The substrate (16 mmol) and $HSiCl_3$ (18 mmol) were added successively to the catalyst (5.10^{-3} mmol) at 0°C, without solvent, under argon. Reaction times and temperatures are given in Table I. The final product was purified by distillation under vacuum (20 mm Hg). 3-(Trichlorosilyl)cyclopentene was then reacted with an excess of EtOH in the presence of Et_3N in ether to afford 3-(triethoxysilyl)cyclopentene. 1-Phenylethyltrichlorosilane was converted into 1-phenylethyltrimethylsilane by reaction with an excess of MeMgBr (3N sol. in ether)

The progress of the catalytic reactions was monitored by ^1H NMR. This showed that, in the case of styrene (entries 4, 5), the palladium complex **2** exhibited high catalytic activity (substrate : **2** = $1:2.10^{-4}$ mol) and high regioselectivity: 1-phenylethyl-trichlorosilane was formed exclusively. In the hydrosilylation of cyclopentadiene (entry 2), the competitive dimerization of the substrate lowered the final yield substantially.

Table I. Hydrosilylation reactions ; see eq.1 and 2.

Entry	[cat]	Substrate	Reaction conditions	Yield (%)	e.e.(%)[c] (config.)
1	$Cl_2Pd(L)_2$, **2**	Cyclopentadiene	25°C, 15h	0[b]	
2			70°C, 30h	26[a]	44 (S)
3	$Cl_2Pd(PhCN)_2$+**1** (1:1)		25/30°C,2h	100[b],70[a]	54 (S)
4	$Cl_2Pd(L)_2$, **2**	Styrene	70°C, 58h	70[b]	
5			90°C, 24h	100[b]	19 (R)
6	$Cl_2Pd(PhCN)_2$+**1** (1:1)		50°C, 24h	100[b]	18 (R)

[a] Isolated yield

[b] By ^1H NMR analysis of the reaction mixture

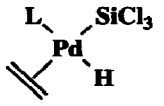
[c] Determined by measurement of optical rotation of known derivatives : 3-(triethoxysilyl)cyclopentene[7] and 1-phenylethyltrimethylsilane[8] respectively.

For comparison, a 1:1 phosphetane-palladium complex was prepared by slow addition of a solution of **1** (5.10^{-3} mmol) in CH_2Cl_2 to Cl_2 Pd $(PhCN)_2$ (5.10^{-3} mmol) at room temperature. After evaporation of the solvent, the crude product was used as a hydrosilylation catalyst. As shown in Table I, this 1:1 complex dramatically increases the reaction rate with respect to the 2:1 complex. The effect is especially striking for cyclopentadiene (entry 3), where a slightly exothermic reaction is observed simply upon mixing the reagents at room temperature.

This phenomenon seems to be general when phosphetane ligands are used; various phosphetane ligands have been tested in catalysts for the hydrosilylation reaction, and a 1:1 phosphine to palladium ratio affords the more effective catalyst precursor in all cases. A detailed study will be reported later. These results indicate that the most active intermediates in the hydrosilylation reaction must be 1:1 phosphine-palladium complexes.

A priori, when using **2** as the catalyst precursor, the reaction could proceed either through a different mechanism to that of the 1:1 catalyst, or via the same intermediates, after decomplexation of a phosphine ligand. The stereochemical outcome of the reactions described above seems to favour the second hypothesis because, within experimental error, both catalysts give the same enantiomeric excesses in styrene hydrosilylation (see Table I). The better asymmetric induction of the 1:1 palladium complex with respect to the 2:1 complex in the hydrosilylation of cyclopentadiene may reflect the lower reaction temperature.[7]

These observations suggest that the same monophosphine-Pd intermediate is operating in the enantiodetermining step, irrespective of the phosphine : metal ratio in the catalyst precursor. Re-coordination of the second phosphetane in a later step of the catalytic cycle, according to the generally postulated mechanism[9], is highly unlikely, given the extremely low concentration of the ligand. The 14-electron complex formed from **3** by olefin insertion into the Pd-H bond could, however, reach the stable 16-electron configuration by η^3 complexation of the allyl moiety, for cyclopentadiene, or by coordination of a second olefin in the case of styrene.



L = phosphine

3

The unexpected improvement of the catalytic reaction by using a phosphine to palladium ratio of 1:1 seems to be peculiar to the phosphetane ligands. In fact, 1:1 or 2:1 ratios of L (L=2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl) to palladium are reported to give almost the same results in the hydrosilylation of 1-octene[2a]. The unprecedentedly strong inhibition of catalysis when **2** is used as the starting material probably reflects the high basicity of the trialkyl phosphine **1**, which slows down the dissociation reaction leading to the catalytically active species.

Our results are in agreement with the findings of T. Hayashi and coworkers[2a], who have recently pointed out a total loss of catalytic activity when chelating bisphosphines are used as ligands. They reasonably argued that a monodentate phosphine (L) leads to a more active square-planar palladium intermediate, **3**, which offers a coordination site for the activation of olefin.

In summary, the results above confirm the assumption of 1:1 phosphine-palladium complexes as intermediates in the palladium-catalyzed hydrosilylation reaction and emphasize a potential inhibitory effect of the second phosphine ligand.

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6. Complex **2** : orange solid ; mp 199°C ; ^{31}P NMR (C_6D_6) δ 62,6 ppm ; selected ^{1}H NMR data : (C_6D_6) δ 0.48 (s, Me), 0.86 (d, $^{3}J_{H-H}$ = 6.7 Hz, Me), 0.96 (d, $^{3}J_{H-H}$ = 5.5 Hz, Me), 1.05 (t, J_{H-P} = 6.5 Hz, P-C-Me), 1.39 (d, $^{3}J_{H-H}$ = 6.5 Hz, Me), 1.60 (t, J_{H-P} = 7.8 Hz, P-C-Me), 2.03 (s, Me), 3.4 (m, 1H, CH_2Ph), 4.0 (m, 1H, CH_2Ph) ppm ; selected ^{13}C NMR data (C_6D_6) δ 17.4 (s, Me), 22.7, 22.8, 23.0, 23.1, 24.2 (t, J_{C-P} = 9.0 Hz, Me), 24.7 (Me), 25.3 (t, J_{C-P} = 5.5 Hz, CH_2), 30.6 (CH), 34.2 (t, J_{C-P} = 5.1 Hz, PCH), 34.5 (CH_2), 35.0 (CH_2), 37.0 (CH_2), 43.1 (CH), 45.7 (C), 46.0 (CH), 50.6 (t, J_{C-P} = 12.9 Hz, P-C), 50.7 (t, J_{C-P} = 13.2 Hz, CH), 142.9 (t, J_{C-P} = 5.1 Hz, C (Ph) .
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